1,042,640

PATENT SPECIFICATION

DRAWINGS ATTACHED

1,042,640

Date of Application and filing Complete Specification: Jan. 28, 1965.

No. 3896/65.

Application made in United States of America (No. 341,068) on Jan. 29, 1964.

Complete Specification Published: Sept. 14, 1966.

Index at acceptance:—C2 C(2B20, 2B40D, 2B40J1, 2B40J4, 2B40K, 2B40L2, 3A8A4, 3A8B1, 3A8B2, 3A8C1, 3A8C2, 3A8D1, 3A8G1, 3A8G3, 3A8K); C3 R(22D1A2, 22D2A2, 22D3B, 22D3D1, 22D3DX, 22N1A, 22N1B)

Int. Cl.:—C 07 d 41/06

COMPLETE SPECIFICATION

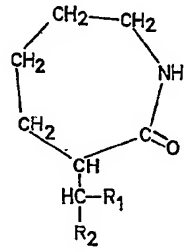
Caprolactam Derivatives and their preparation

We, ALLIED CHEMICAL CORPORATION, a Corporation organized and existing under the laws of the State of New York, United States of America, of 61 Broadway, New York 6, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention provides new derivatives of ε-caprolactam and polyamides produced therefrom.

Although ε-caprolactam is readily polymerisable to form useful polymers (generally known as nylon 6), derivatives of ε-caprolactam in which one of the hydrogen atoms attached to a carbon atom of the lactam ring is replaced by an organic radical are not generally polymerisable. Thus, for example, it is extremely difficult, if not impossible, to polymerise *alpha*-ethyl and *alpha*-propyl ε-caprolactam. In many applications it is desirable to employ polyamide polymers having functional organic groups attached to the polyamide chain. These functional groups make possible various gradations in the physical and chemical properties of the polymer which are unobtainable by other methods. Although mixed co-polyamides have been prepared using one monomer containing such functional organic groups, the simpler expedient of polymerising a substituted lactam to obtain nylon 6 polymers having functional organic groups attached to the polyamide chain has not hitherto been accomplished.

It has now been found that high molecular weight poly-amides ranging from soft and soluble resins, to hard and insoluble resins may be produced by the polymerisation of *alpha*-substituted ε-caprolactam derivatives represented by the formula:



wherein R_1 is a carboxy, alkoxycarbonyl, cyano carbamoyl or acyl group and R_2 is an electron-attracting group (as hereinafter defined) or a hydrogen atom and R_1 and R_2 may be the same or different. R_2 is preferably a carboxy, alkoxycarbonyl, cyano or carbamoyl group. The *alpha*-substituted ε-caprolactam derivatives of the above formula are new compounds and as such represent an embodiment of the invention. Preferred such compounds are: α-(diethoxycarbonylmethyl)caprolactam; α-(dicarboxymethyl)caprolactam; α - (carboxymethyl)caprolactam; α - (ethoxycarbonylmethyl)caprolactam; α-carbamoylmethyl)caprolactam and α - (cyano - ethoxy - carbonylmethyl)caprolactam.

An electron-attracting group is for the purpose of this specification, defined as a group which, when directly joined to a benzene nucleus, causes nucleophilic substitution in the *meta*-position of the ring to the extent that at least 40 percent of the substituted product is the *meta*-isomer. *Meta*-directing electron-attracting groups of this type are described in "Organic Chemistry" by Fieser and Fieser, 2nd Edition, page 595 (D.C. Heath and Company) and Chemistry of Organic Compounds,

Noller, 2nd Edition, pages 441—2 (W. B. Saunders Company) and include tri-alkyl-ammonium, alkyl sulphonyl, nitro, cyano, carboxy, formyl, sulpho, alkoxycarbonyl, carbamoyl, trichloromethyl, acetyl, nitro-methyl and ammonium, represented respectively by the formula: $—NR_2^+$, $—SO_2R$, $—NO_2$, —CN, —COOH, —CHO, $—SO_3H$, —COOR, $—CONH_2$, CCl_3, $—COCH_3$, $—CH_2NO_2$ and $—NH_3^+$, wherein R is a lower alkyl group, preferably of 1 to 4 carbon atoms.

The new *alpha*-substituted ε-caprolactam derivatives of this invention may conveniently be prepared by condensing an *alpha*-halogenated ε-caprolactam with a metallo-organic compound containing at least one *meta*-directing electron attracting group as hereinbefore defined or a chemical precursor capable of being converted into such a group. The *alpha*-halogenated ε-caprolactam may be prepared in any known manner such, for example, as that described in J. Amer. Chem. Soc., *80*, 6238 (1958). The bromine derivative is generally preferred in view of its greater reactivity during the condensation reaction, but other halogen derivatives are suitable, especially the chlorine one which is economically advantageous.

The metallo-organic compounds used in the above method are of the formula $M—\underset{\displaystyle R_2}{\overset{\displaystyle |}{CH}}—R_1$, wherein M is an alkali metal and R_1 and R_2 are as hereinbefore defined. They are prepared by the metallization of compounds which, because of tautomerism of resonance stabilization, possess a hydrogen atom attached to carbon which is replaceable by an alkali metal. Typical examples of compounds containing the replaceable hydrogen atom include malononitrile, malonic esters, acetoacetic esters, acetylacetone, nitromethane, cyanoacetic esters, and other compounds analogous thereto containing activated methyl or methylene groups. The metallo-organic compound is generally prepared by treating the organic compound containing the replaceable hydrogen atom with an alkali metal such as, for example, lithium, sodium or potassium, under anhydrous conditions. Preferred metallo-organic compounds are sodio diethyl malonate or sodio ethyl cyanoacetate.

The condensation of the *alpha*-halogenated ε-caprolactam and the metallo-organic compound is preferably carried out under anhydrous conditions in an inert solvent medium. Temperatures of between 50° C. and 200° C. may be employed with temperature control effected by reflux condensers or other suitable means. Reaction times of from 2 to 30 hours generally provide the new *alpha*-substituted ε-caprolactam in yields of 50% or more. The reaction product is isolated from the reaction mixture by solvent evaporation, and washing and recrystallisation of the non-volatile residue. The new *alpha*-substituted ε-caprolactam derivatives are white crystalline solids, which are soluble in various polar and non-polar organic solvents. They are identified by conventional methods of analysis such as elemental analysis, infra-red spectrophotometric analysis, molecular weight determination, and chemical transformations.

Certain of the new ε-caprolactam derivatives may also be prepared by chemical reaction carried out on other ε-caprolactam derivatives containing *meta*-directing electron attracting groups or chemical precursors capable of being converted into a *meta*-directing electron attracting group. In still further chemical transformations, the monomers of this invention may be converted into other useful compounds such as derivatives of amino caproic acid, and molecules containing 2 ε-caprolactam rings.

The production of polymers from the ε-caprolactam derivatives of this invention may be accomplished by procedures similar to those generally known for the preparation of high molecular weight polyamides from ε-caprolactam. The polymerisation is usually carried out at temperatures between 75° and 300° C., preferably in an inert atmosphere. The polymerisation may be carried out in the presence of catalysts, viscosity stabilizers, anti-oxidants, pigments, fillers, foaming agents, plasticizers, and other additives commonly employed in the production of polymer compositions. Other monomer species, polymerisable under the applied reaction conditions or polymerisable thereafter by suitable activation, may also be present. Depending upon the composition of the reaction mixture, the polymerisation reaction is completed within from a few minutes to 20 hours. The polymer product may be purified and further processed by conventional methods.

Referring to the accompanying drawings, Figure 1 is an infra-red adsorption spectrum of the product obtained in Example 1 below, and Figures 2, 3, 4 and 5 are the infra-red spectra of the products of Examples 3, 4, 5 and 6 respectively.

The following Examples serve to illustrate the invention. All parts and percentages are by weight unless otherwise specified.

EXAMPLE 1.

α-(Diethoxycarbonlymethyl)caprolactam

600 ml. of anhydrous ethanol were placed into a 3 litre three-necked flask equipped with a stirrer, dropping funnel and a reflux condenser carrying a drying tube. With frequent cooling, 23 g. of sodium were added in large pieces. The solution was heated under gentle reflux and 400 g. of redistilled diethyl malonate were added over a period of one hour. The heating was continued for three hours after the addition was complete. After this time 192 g. of α-bromocaprolactam dissolved in 300 ml.

dry benzene were added. The reaction mixture was then heated under reflux for 5 hours and allowed to stand at room temperature overnight. The ethanol was then removed under aspirator vacuum. The remaining solution was washed with 400 ml. 10% aqueous hydrochloric acid. The aqueous phase was extracted several times with diethyl ether. The diethyl ether was combined with the organic phase and washed with a concentrated solution of sodium bicarbonate and water, and then dried over anhydrous sodium sulphate. After removal of the solvents and excess malonic ester under vacuum, the reaction product was recrystallised from *n*-hexane. The dried crystals had a melting point of 94—96° C., and weighed 175 grams, representing a yield of 65%. Elemental analysis of the product was as follows:

Calculated:
57.55% C; 7.8% H; 5.16% N
Found:
57.70 7.76 5.46.

The infra-red absorption spectrum of the product is shown in Figure 1 of the accompanying drawings.

EXAMPLE 2.

α-(Dicarboxymethyl)caprolactam

67.5 g of potassium hydroxide were dissolved in 250 ml. 99.8 ethanol. To this solution were added 135.6 g. of α-(diethoxycarbonylmethyl)caprolactam (prepared as in Example 1) dissolved in 150 ml. of ethanol. The resulting solution was heated under reflux for 20 hours. After cooling, the precipitated dipotassium salt was collected and washed first with ethanol and then with diethyl ether. The yield was 141.7 g (97.5%).

The dipotassium salt was dissolved in 100 ml. water. The solution was extracted with diethyl ether, cooled below 0° C., and acidified with concentrated hydrochloric acid keeping the temperature at 0° C.

The precipitate was collected and washed with a small quantity of cool methanol and diethyl ether. 110 g. of dry crystalline product were obtained. The crystals melt with decomposition at 160° C. For the purpose of analysis a small portion was recrystallised from methanol. Elemental analysis of the product was as follows:

Calculated:
50.23% C; 6.09% H; 6.51% N
Found:
50.28 6.13 6.33, 6.50.

EXAMPLE 3.

α-(Carboxymethyl)caprolactam

21.52 g. of α-(dicarboxymethyl)caprolactam (prepared as in Example 2) was added in small portions to 150 ml. of *o*-dichloro-benzene at 160—165° C. The resulting clear solution was hot filtered from some resinous by-products. Upon cooling, the product crystallised, providing a yield of 11.4 g. (67%). The product recrystallised from hot *o*-dichlorobenzene, had a melting point of 176—177° C. Elemental analysis of the product was as follows:

Calculated: 56.13% C; 7.65% H; 8.18% N
Found: 56.05 7.57 8.26

The infra-red absorption spectrum of the product is shown in Figure 2 of the drawings.

EXAMPLE 4.

α-(Ethoxycarbonylmethyl)caprolactam

34.24 g. of α-carboxymethyl)caprolactam (prepared as in Example 3) were dissolved in a mixture of 120 ml. ethanol, 20 ml. benzene and 2 ml. concentrated sulphuric acid. This solution was refluxed in an esterification apparatus for 4 hours. The excess solvent was removed by distillation and the residue dissolved in diethyl ether. The diethyl ether solution was washed with saturated sodium bicarbonate solution and dried over anhydrous sodium sulphate. The diethyl ether was removed in vacuum and the crystalline residue recrystallised from n-hexane giving a yield of 29.3 g. (74%). The crystalline product had a melting point of 76.5—77.5° C., and its elemental analysis was as follows:

Calculated:
60.28% C; 8.6% H; 7.03% N
Found:
60.29 8.65 7.00

The infra-red absorption spectrum of the product is shown in Figure 3 of the drawings.

EXAMPLE 5.

α-(Carbamoylmethyl)caprolactam

19.93 g. of the α-(ethoxycarbonylmethyl)-caprolactam (prepared as in Example 4) was dissolved in 150 ml. concentrated aqueous ammonium hydroxide. The solution was allowed to stand for 48 hours at room temperature. It was then distilled under vacuum and the residue recrystallised from ethanol giving a yield of 11.1g. (65%). The crystalline product had a melting point of 202.3° C., and an elemental analysis as follows:

Calculated:
56.45% C; 8.29% H; 16.46% N
Found:
57.34 8.49 16.01.

The infra-red absorption spectrum of the product is shown in Figure 4 of the drawings.

EXAMPLE 6.

α-(Cyano-ethoxycarbonylmethyl)caprolactam

A dispersion of 46 g. of sodium was prepared in 2 litres of toluene. The toluene was then replaced by anhydrous ethyl ether. To this dispersion was then added a solution of 500 g. of ethyl cyanoacetate dissolved in 700 ml. of diethyl ether. The reaction mixture was held for 24 hours at room temperature, during which time all sodium reacted. To this mixture were then added 380 g. of α-bromo-caprolactam dissolved in 1200 ml. benzene. After the addition the reaction mixture was

heated under reflux for 24 hours, after which the reaction mixture was worked up as described in Example 1 for α-(diethoxycarbonylmethyl)caprolactam. α-Cyano-ethoxycarbonylmethyl)-caprolactam was obtained in a yield of 232 g. (54%). The crystalline product had a melting point of 153° C., and an elemental analysis as follows:

Calculated:

58.91% C; 7.19% H; 12.49%N

Found:

59.02	7.32	12.79
59.25	7.37	12.91

The infra-red absorption spectrum of the product is shown in Figure 5 of the drawings.

The infra-red analyses of the products of Examples 1 and 3 to 6 were carried out with a Perkin-Elmer double beam spectro-photometer, Model 21, equipped with a sodium chloride prism. The spectra were recorded as solids in potassium bromide wafers and are given in the accompanying drawings as optical density plotted against wavelength of the incident beam in microns.

Referring to the drawings, it will be noted that all the spectra in Figures 1 to 5 show bands in the 3.2—3.3 micron and 3.1—3.15 micron regions. Stemming from N—H stretching vibrations, these bands are typical of cyclic lactams. All spectra show the amide I band in the 6.0 micron region which is typical for the carbonyl absorption of cyclic lactams consisting of unstrained length of 6 or more carbon atoms. In the case of α-(carboxymethyl)-caprolactam (Figure 2) this band occurs at 6.15 microns. In the spectra of all compounds except that of α-(carbamoylmethyl)-caprolactam (Figure 4) the so-called amide II band at 6.2 microns is missing. Its occurrence in the spectrum of the latter compound is expected because of the presence of a primary amide group. All compounds absorb in the 7.7—8.4 micron region causing the so-called amide III band. The spectra in all of the Figures show an intense band in the 5.7—5.8 micron region which in the case of the α-(diethoxycarbonylmethyl)caprolactam (Figure 1) has been split into two bands at 5.7 and 5.8 microns. Absorption in that region is attributed to C=O stretching vibrations, while the bands in the 9.6—9.8 micron and the 8.4 micron regions stem from C—O stretching vibrations.

The spectrum of α-(carbamoylmethyl)caprolactam (Figure 4) shows, in addition to the amide II band, a band at 7.1 microns which may be assigned to C—N stretching absorption. This band is missing in *N*-substituted amides.

The spectrum of α-(carboxymethyl)caprolactam (Figure 2) shows a broad band at 4.0 microns assigned to OH stretching vibrations. The spectrum of this compound exhibits another broad band at 5.2 microns which is not present in the spectra illustrated for the other caprolactam derivatives, Absorption in this region has been observed for most amido acids.

The spectrum of α-(cyano-ethoxycarbonylmethyl)caprolactam (Figure 5) shows the amide I and amide III bands at 6.0 and 8.1 microns, respectively, and an intense band at 4.43 microns. The latter has been assigned to C≡N stretching vibrations.

Examples 7 to 12 which follow illustrate the production of polyamides from the new ε-caprolactam derivatives of this invention.

EXAMPLE 7.

10 g. of α-(carboxymethyl)caprolactam (prepared as in Example 3) are placed in a test tube. The system is flushed repeatedly with nitrogen and then heated at 225° C. for 1 hour maintaining a nitrogen atmosphere. After that time a colourless, transparent, hard polymer forms, having the shape of the test tube. This polymer does not melt or decompose at temperatures below 300° C., and is insoluble in all common solvents.

EXAMPLE 8.

Equal parts of α-(carboxymethyl)caprolactam (prepared as in Example 3) and α-(ethoxycarbonylmethyl)caprolactam (prepared as in Example 4) are heated in a nitrogen atmosphere at 255° C. for 8 hours. The polymer which forms is a transparent, soft material which starts to flow at 110° C., and melts without any signs of decomposition at 160° C. The polymer is soluble in organic solvents such as chloroform, benzene and acetic acid.

EXAMPLE 9.

Equal parts of α-(carboxymethyl)caprolactam and ε-caprolactam are heated in a nitrogen atmosphere at 255° C. for 20 hours. The polymer which forms is translucent. It softens at 218° C. and melts at 242° C.

EXAMPLE 10.

19 parts of ε-caprolactam, 1 part of ε-aminocaproic acid and 0.096 part of α-(carboxymethyl)caprolactam are placed in a stirred reactor and heated for 5 hours at 255° C. The polymer which forms is extruded, washed with hot water, dried and spun to fibres. These fibres are drawn without breaking at a drawing ratio of 1:6. The tensile strengths of the drawn fibres are found to be 10.5—11.0 grams per denier, and the corresponding elongations are 11—12%.

EXAMPLE 11.

Equal parts of α-(diethoxycarbonylmethyl)-caprolactam (prepared as in Example 1) and water are placed in an autoclave and heated at 270° C., maintaining a pressure of 20 atmospheres of nitrogen for 2 hours. After that time the pressure is released and the reaction product is heated for an additional 2 hours at 270° C. in a nitrogen atmosphere. The poly-

mer thus obtained is a transparent, hard material which softens at 95° C. and melts at 130° C.

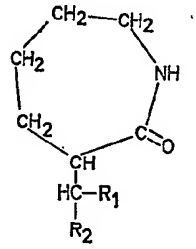
EXAMPLE 12.

8 parts of hexamethylene diammonium adipate, 2 parts of α-(carboxymethyl)caprolactam (prepared as in Example 3), and 10 parts of water are placed in an autoclave and heated at 280° C., maintaining a pressure of 20 atmospheres of nitrogen, for 2 hours. After that time the pressure is released and the reaction mixture is heated for an additional 2 hours at 280° C. in a stream of nitrogen at atmospheric pressure. The polymer thus produced is a hard crystalline material which melts at 230° C.

The polymers of this invention are polyamides having functional organic groups attached to the polyamide chain. They may be employed in the production of end products such as adhesives, coating compositions, textile yarns, tyre yarns, bristles, films, moulded products, and other shaped articles. Such end products may be chemically modified by reactions of the groups R_1 or R_2, and may be subjected to commonly employed treatment processes such as dyeing, embossing, printing, irradiation, drawing, machining, laminating, and other conventional operations.

WHAT WE CLAIM IS:—

1. α-Substituted caprolactam derivatives of the formula:



wherein R_1 is a carboxy, alkoxycarbonyl, cycano, carbamoyl or acyl group and R_2 is an electron attracting group (as hereinbefore defined) or a hydrogen atom and R_1 and R_2 may be the same or different.

2. α-Substituted caprolactam derivatives as claimed in claim 1 in which R_2 is a carboxyl, alkoxycarbonyl, cyano or carbamoyl group.

3. α - (Diethoxy - carbonylmethyl)caprolactam.

4. α-(Dicarboxymethyl)caprolactam.

5. α-(Carboxymethyl)caprolactam.

6. α-(Ethoxycarbonylmethyl)caprolactam.

7. α-(Carbamoylmethyl)caprolactam.

8. α-(Cyano-ethoxycarbonylmethyl)caprolactam.

9. α-Substituted caprolactam derivatives according to claim 1 substantially as described in Examples 1 to 6 and with reference to the accompanying drawings.

10. A process for the production of α-substituted caprolactam derivatives as claimed in any of claims 1 to 9, which comprises condensing an α-halogenated caprolactam with a metallo-organic compound of the formula $M—CH(R_2)—R_1$, wherein M is an alkali metal, and R_1 and R_2 have the meanings given in claim 1, followed, if desired, by the conversion of the compound thus produced into another compound according to claim 1 in manner known *per se*.

11. A process according to claim 10, wherein the metallo-organic compound is sodio diethyl malonate or sodio ethyl cyanoacetate.

12. A process according to claim 10 or 11, wherein the α-halogenated caprolactam is α-bromocaprolactam.

13. A process according to claim 10, substantially as hereinbefore described in Examples 1 to 6.

14. α-Substituted caprolactam derivatives when prepared by the process of any of claims 10 to 13.

15. A process for the production of polyamides which comprises polymerising an α-substituted caprolactam derivative as claimed in any of claims 1 to 9 or 14 either alone or with at least one monomer copolymerisable therewith.

16. A process according to claim 15, substantially as described in any of Examples 7 to 12.

17. Polyamides when prepared by the process of claim 15 or 16.

J. A. KEMP & CO,
Chartered Patent Agents,
14 South Square,
Gray's Inn, London, W.C.1.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1966. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

Fig. 1.

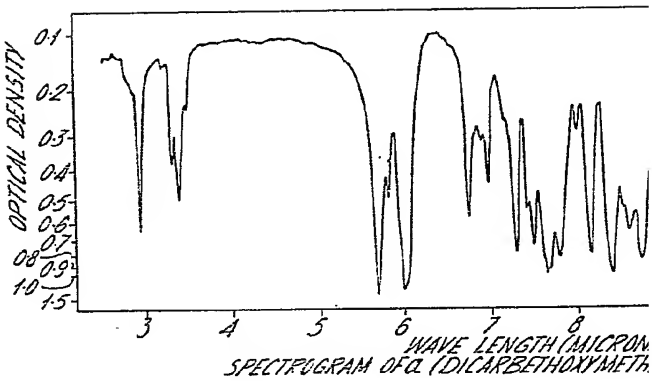


Fig. 2.

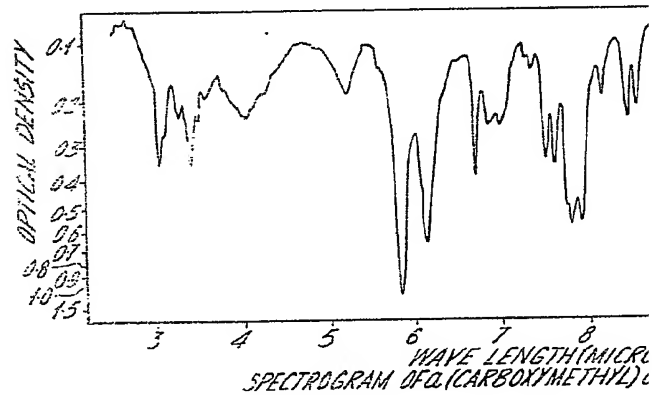
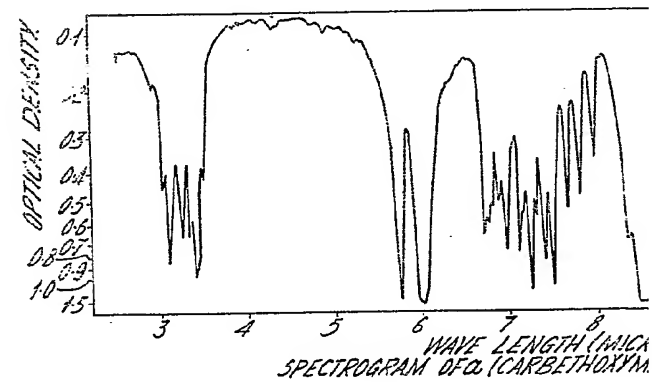


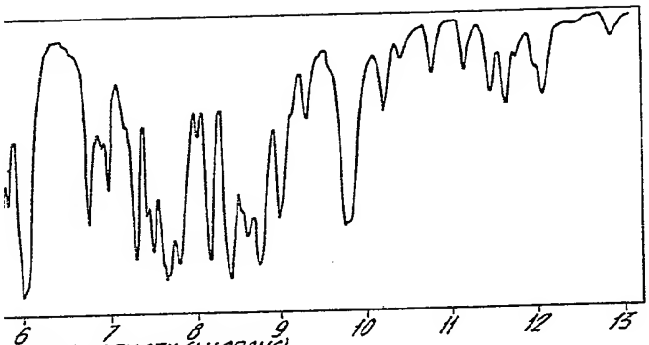
Fig. 3.



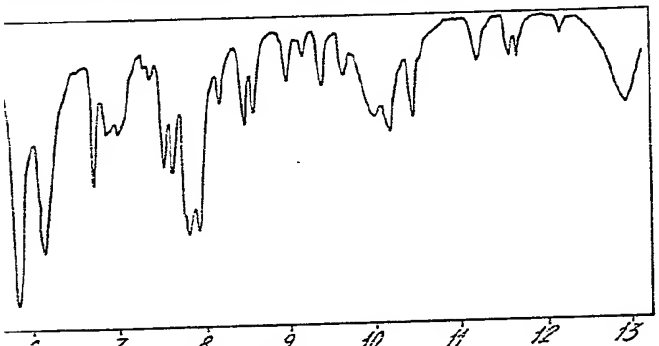
1042640 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

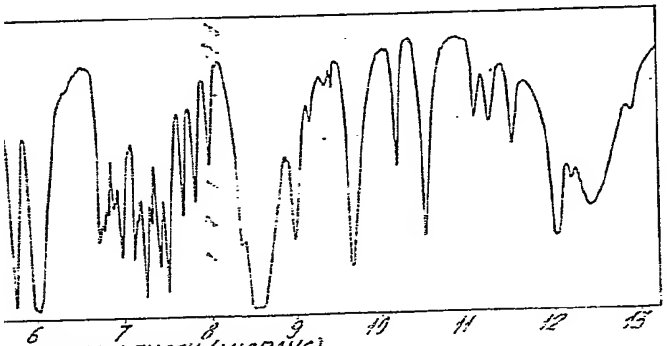
Sheet 1



ΩFα (DICARBETHOXYMETHYL) CAPROLACTAM



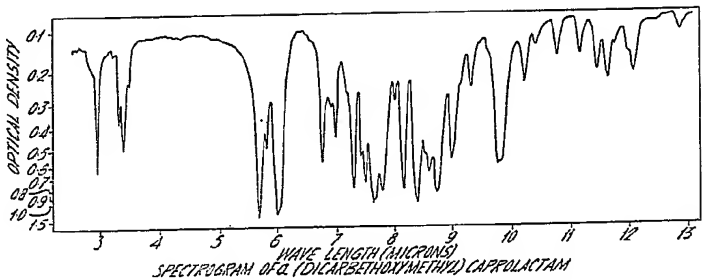
OFα (CARBOXYMETHYL) CAPROLACTAM



ΩAM OFα (CARBETHOXYMETHYL) CAPROLACTAM

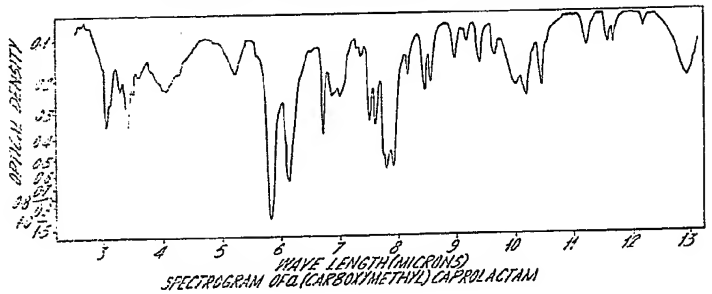
1042640 COMPLETE SPECIFICATION
2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 1

Fig. 1.



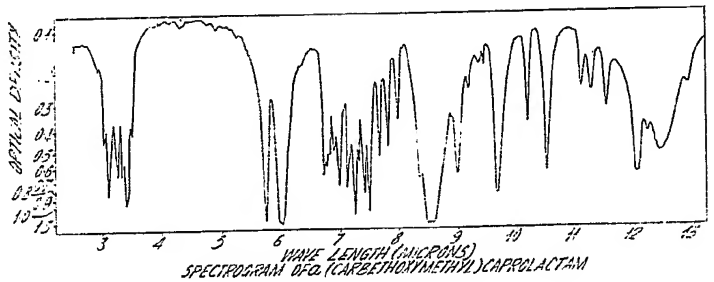
SPECTROGRAM OF α (DICARBETHOXYMETHYL) CAPROLACTAM

Fig. 2.



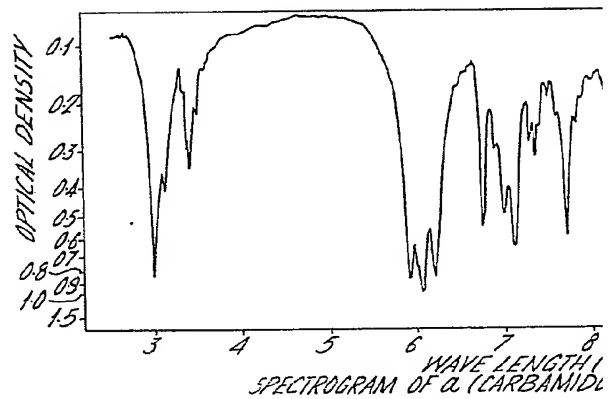
SPECTROGRAM OF α (CARBOXYMETHYL) CAPROLACTAM

Fig. 3.



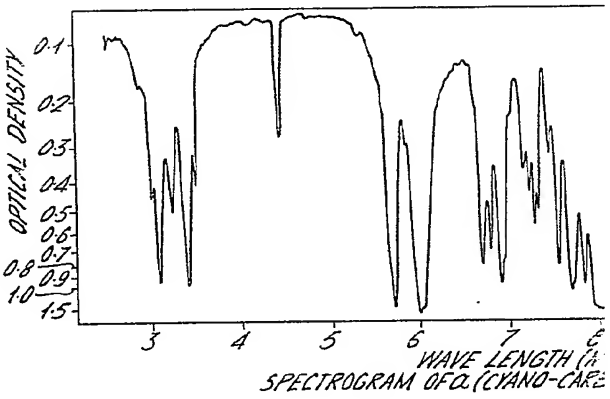
SPECTROGRAM OF α (CARBETHOXYMETHYL) CAPROLACTAM

Fig.4.



SPECTROGRAM OF α (CARBAMIDO

Fig.5.

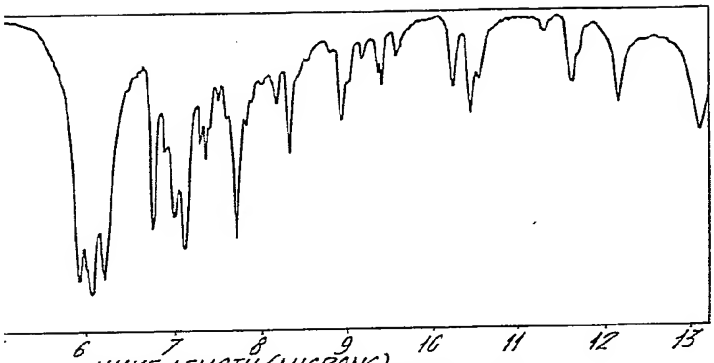


SPECTROGRAM OF α (CYANO-CARB

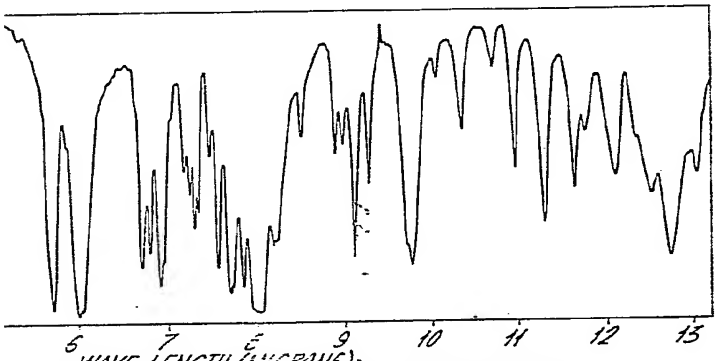
1042640 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 2



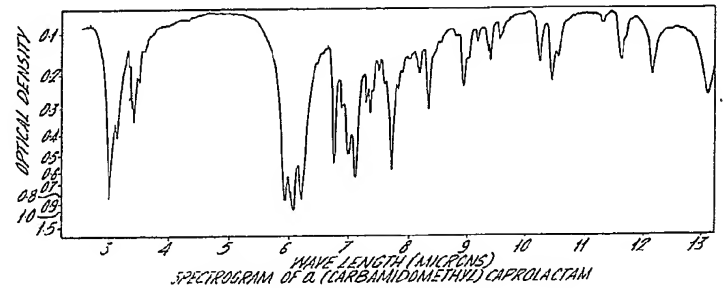
GRAM OF α (CARBAMIDOMETHYL) CAPROLACTAM



OGRAM OF α (CYANO-CARBETHOXYMETHYL) CAPROLACTAM

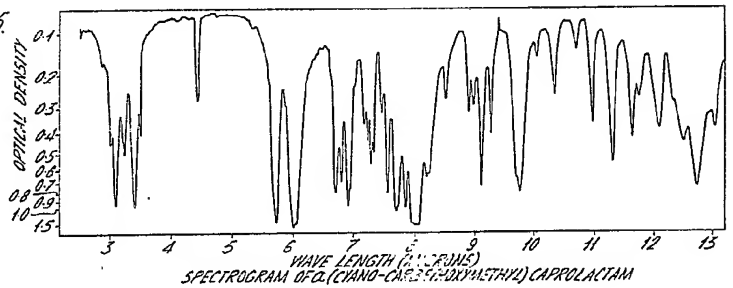
1042640 COMPLETE SPECIFICATION
2 SHEETS This drawing is a reproduction of the Original on a reduced scale
Sheet 2

Fig.4.



SPECTROGRAM OF α (CARBAMIDOMETHYL) CAPROLACTAM

Fig.5.



SPECTROGRAM OF α (CYANO-CARBOXYMETHYL) CAPROLACTAM